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Identification of Spatial and Temporal Patterns of Coastal Waters in Sanya Bay, South China Sea by Chemometrics

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ABSTRACT. Anthropogenic influence and natural processes exert important effects on the aquatic ecosystem of Sanya Bay in the northern part of the South China Sea. These effects result to the temporal and spatial differences of water quality in the bay. In this study, four-way principal component analysis is employed to identify the natural characteristics of the water in this bay, as well as the anthropogenic effects on its water quality. The results indicate that anthropogenic influence (nutrients as indicator) is the dominant factor that affects the water quality at the mouth of Sanya River (S1). This region exhibits the maximum effects of the discharge from Saya River, which is indicated by higher nutrient levels and Chl a than in outer bay. Both upwelling and mixing caused by monsoons are the dominant factors that affect water quality in the central and outer bays. The water exchange between the bay and open oceanic water exercises an important effect on the water quality in Sanya Bay. The information on the spatial and temporal variations of the water quality in Sanya Bay may be valuable for the socioeconomic development and human health in this area.

Keywords: anthropogenic influence, nature processes, nutrients, heavy mental, chemometrics

1. Introduction

Given the sudden increase of population and rapid economic development in littoral areas, coastal waters have received large amounts of pollution from various sources, such as recreation, fish culture, and toilet flushing (Bowen and Depledge, 2006; Kuppusamy and Giridhar, 2006). Coastal waters are facing many ecological problems, such as eutrophication and pollution (Huang et al., 2003). Hence, preventing and controlling marine water pollution, as well as regularly implementing monitoring programs that help understand the spatial and temporal variations in coastal water quality are necessary. Coastal water characteristics are largely determined by a number of factors, including climatic conditions, interaction between land and ocean, and anthropogenic activities.

Chemometrics can offer various methods that can be successfully applied for data exploration and modeling in environmental studies because environmental data sets are multidimensional and have a complex structure. Environmental data sets require the extraction of relevant information hidden in the data to provide an overview about the processes in the studied system.

Chemometrics has been widely employed in identifying the temporal and spatial variation and sources of pollution in coastal waters (Chau and Muttil, 2007; Dong et al., 2010a; Dong et al., 2010; Kuppusamy and Giridhar, 2006; Simeonov et al., 2003; Singh et al., 2004; Wang et al., 2006; Wu et al., 2011a; Wu et al., 2011b; Yeung, 1999; Yung et al., 2001; Zhou et al., 2007). Coastal water quality monitoring data sets, exhibiting multi-dimensional structure (space, time, variables, and layers), require multi-way analysis methods, e.g., the four-way principal component analysis (PCA), to explore and extract the data structure and their relationships.

In this paper, four-way principal component analysis is applied to identify the natural characteristics of the waters in Sanya Bay and the anthropogenic influence on its water quality. In addition, the environmental information contained in a wide data set of its waters is also summarized. These results may help regional environmental protection agencies assess the marine water quality in Sanya Bay and control the pollution in the area.

2. Materials and Methods

2.1. Study Area

Sanya Bay is a tropical bay in the southern part (from 109° 20' to 109° 30' E, 18° 11' to 18° 18' N) of Hainan Island, China, with a water area of 120 km^2 and an average depth of 16 m. Dongmao Island, Ximao Island, and Luhuitou are composed of mostly coastal coral reefs. The Sanya River is in the eastern part of the bay (length of 31.3 km, drainage area of 337 km^2,

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and annual flow of 2.11×10^9 m^3) (Huang et al., 2003). The wet and warm southwest monsoon prevails during the wet season, from April to September, which brings humid air from low latitudes, resulting in gentle monsoonal rainfall in spring and heavy rainfall in summer. By contrast, a dry and cold northeast monsoon predominates during the dry season, from October to March.

Thirteen stations were chosen for monitoring the activities in Sanya Bay (Figure 1) to evaluate the natural and anthropogenic status of the bay.

2.2. Sampling and Analytical Methods

Water samples were collected from the surface (0.5 m below the surface) and bottom (depth: 1.0 m from the bottom) layers of all stations in January (winter), April (spring), August (summer), and November (autumn) in 2010. A Quanta® water quality monitoring system (Hydrolab Corporation, USA) was used to collect the data for temperature (T/°C), pH, salinity (S/PSU), and specific conductivity (SPC) at the surface and bottom layers. Seawater samples for nutrient analysis were collected on the surface layer using 5 L GO FLO bottles, according to the methods and sampling tools of "The specialties for oceanography survey" (GB12763-91, China). The water samples from the surface layer were analyzed for nitrate (μmol NO_3-N·L^{-1}), nitrite (μmol NO_2-N L^{-1}), and silicate concentrations (μmol SiO_3-Si·L^{-1}) using a SKALAR auto-analyzer (Skalar Analytical B.V. SanPlus, Holand). Ammonium concentration (μmol NH_4-N·L^{-1}) was analyzed using the hypobromite oxidation method. Phosphorus concentration (μmol PO_4-P·L^{-1}) was analyzed using the methods of oxidation by molybdophosphoric blue. The dissolved oxygen concentration (DO/mg·L^{-1}) was determined using Winkler titration. Water quality parameters were measured according to the reference (Grasshoff et al., 1999; Wu et al., 2009). Heavy metals (Pb, Cu, Zn, and Cd) were determined using atomic absorption spectrometry (GB12-763-91, China).

2.3. Data Analysis

2.3.1. One-way Analysis of Variance (ANOVA)

One-way ANOVA tests the null hypothesis that two or more population means are equal. The question was whether (H_0) the population means are equal for all groups, and that the observed differences in the sample means are due to random sampling variation, or (H_a) the observed differences between the sample means are due to actual differences in the population means.

In this study, the differences between surface and bottom layer were identified by one-way ANOVA.

2.3.2. Four-Way Data Analysis

In this study, the data were arranged in a four-way array, X, of dimensionality 13 (monitoring sites) × 21 (parameters) × 4 (seasons) × 2 (sampling layers). Monitoring sites, parameters, seasons, and sampling layers constituted the modes of the array. Such type of data can be modeled using PARAFAC and Tucker3 methods extended to four-way array (Singh et al., 2006; Stanimirova and Simeonov, 2005).

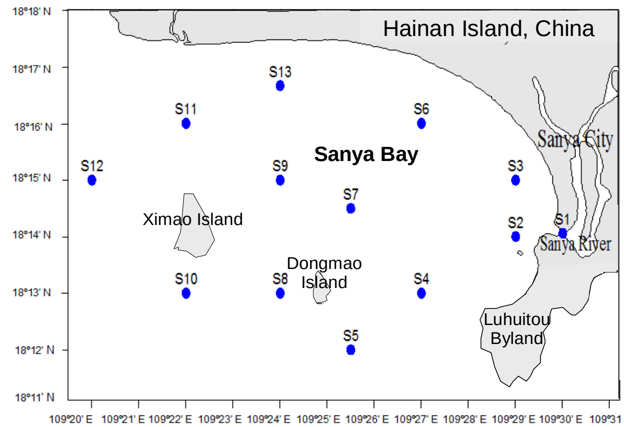

Figure 1. Monitoring stations in Sanya Bay.

In the four-way Tucker3 model, the original four-way data array, $X(I \times J \times K \times L)$ is decomposed into four loading matrices, $A(I \times P)$, $B(J \times Q)$, $C(K \times R)$, $D(L \times S)$, and a core matrix, G , as shown below:

$$x_{ijkl} = \sum_{p=1}^{P}\sum_{q=1}^{Q}\sum_{r=1}^{R}\sum_{s=1}^{S} a_{ip} b_{jq} c_{kr} d_{ls} g_{pqrs} + e_{ijkl} \qquad (1)$$

where a_{ip}, b_{jp}, c_{kr}, and d_{ls} are the elements of the loading matrices; A, B, C, and D of $(I \times P)$, $(J \times Q)$, $(K \times R)$, and $(L \times S)$ dimensions, respectively (I = sampling sites, J = variables, K = monitoring time (season), and L = sampling layers [surface and bottom]). The loadings for each matrix are as follows: matrix A for different monitoring sites, matrix B for each of the parameters, matrix C for seasons, and matrix D for the different sampling layers. A, B, C, and D are orthogonal. g_{pqrs} stands for elements (p, q, r and s) of the core matrix G and e_{ijkl} is the error term of the j-scaled X data array. The elements (g_{pqrs}) of the core reflect the interactions among the four modes (A, B, C, and D) and P, Q, R and S are the number of factors extracted from the four different modes, selected as small as possible (Singh et al., 2006; Stanimirova and Simeonov, 2005). As the original data unfold to $S(I \times JKL)$, the four-way Tucker model can be presented as follows:

$$X^{(I \times JKL)} = AG(D \otimes C \otimes B)^T + E \qquad (2)$$

where $\otimes$ is the Kronecker product, E is the matrix of the model residuals, and G is the core array: $G(P \times Q \times R \times S)$ arranged as $P \times QRS$. The major advantage of using the Tucker3 model is its flexibility in choosing different number of factors in different modes and possible interactions between the loadings.

Different methods, such as split-half analysis (Harshman and De Sarbo, 1984) and residual analysis (Bro, 1998) can be used to obtain the optimal model and verify its suitability to the studied data. The core consistency diagnostic (Bro and Kiers, 2003) was used in this study.

All the mathematical and statistical computations were performed using MATLAB2010a (Mathworks Inc., USA).

3. Results

The surface water temperature at the sampling stations reflected the seasonal change in air temperature (Figure 2). The surface water temperature had a broad range (from 23 to 30 °C), with its maximum in July and its minimum in January. The temperature difference between winter and summer was significant ($p < 0.05$). The surface salinity at the sampling stations was less than 32 psu in October because of rainfall. Low salinity levels were recorded at S1 located near the mouths of Sanya River (Figure S1). DO content ranged from 5.62 mg L^{-1} to 12.18 mg L^{-1}, while pH ranged from 7.70 to 8.25.

Figure S2 shows the temporal and spatial variations in nutrient concentrations. Nitrate concentration varied between 0.38 and 8.93 $\mu mol \cdot L^{-1}$ (Figure S2), while the ammonia concentration between 0.91 and 5.78 $\mu mol \cdot L^{-1}$ during the study period. The concentration of each inorganic nitrogen species was higher at S1 than at the other monitoring sites (S2 ~ S13). Phosphate and silicate concentrations ranged from 0.08 to 0.96 $\mu mol \cdot L^{-1}$ (Figure S3), and from 3.00 to 5.45 $\mu mol \cdot L^{-1}$ (Figure S4), respectively. Phosphate and silicate concentrations in July and October were more than those in January and April.

Chlorophyll concentration ranged from 0.19 $\mu mol \cdot L^{-1}$ to 53.31 $\mu g \cdot L^{-1}$, and was higher at S1 than in the other monitoring sites (S2 ~ S13). The Chl a concentration at the bottom layer increased sharply and significantly exceeded that on the surface layer in July (Figure S5).

The result of the concentration of Cu in the water column of the bay indicated the distinct season change ($p < 0.05$). The concentrations of Zn, Cd, Pb, and Cu increased from the outer bay to the inner bay near the Sanya River mouth. Figure S6 shows the spatial and seasonal changes of Cu in Sanya Bay.

Four-Way Data Analysis

The Tucker3 model with optimal complexity considered was (3, 2, 2, 2), that is, three components in mode A (sampling sites), two components in mode B (variables), two components in mode C (seasons), and two components in mode D (layers). This model explained 39.7% of variance. In the plot of the stations (Figure 3a), all the stations (S3 ~ S13) showed negative values in the first component (A1), and were spread along the second component (A2). The S1 in the Sanya River estuary area is away from other stations (S2 ~ S13), where nutrients were low. This direction also corresponded to a decrease in salinity.

The loading plot of variables in the first two components (B1 and B2) is shown in Figure 3b. The loadings of the nutrients in the first two components (B1 and B2) were positive. High negative loadings on pH in mode B1 can be explained with high levels of dissolved organic matter that consumes large amounts of oxygen, which undergoes anaerobic fermentation processes, leading to the formation of ammonia and organic acids. The hydrolysis of these acidic materials causes a decrease of pH (Singh et al., 2004; Vega et al., 1998). Pollution indicator variables (nutrients) exhibited positive loadings in mode B1. Therefore, B1 represented variables indicating anthropogenic pollution.

Temporal information is described in terms of loadings of each sampling month on the two components of the sampling time mode, as shown in Figure 3c. Loadings in October exceeded 0.7 in mode C2. Heavy rainfall occurred before the sampling time. Loadings at the surface and bottom layers were positive and negative in D2 (Figure 3d), respectively. Differences in water quality between the surface and bottom layers exist.

4. Discussion

4.1. Comparison with Classical and Four–Way PCA

PCA loading plots are easy to interpret, whereas PCA score plots are extremely difficult to analyze due to a large number of objects and the fact that two modes, namely, time and depth, are mixed (Dong, et al., 2010b). These difficulties can be overcome by applying the Tucker 3 approach, which allows the investigation of the three modes separately. This approach requires the organization of the data into a four-way array, X (13 ×21 × 4 × 2). The loading plots, obtained as a result of the Tucker3 analysis, are presented in Figure S5. The core matrix G is necessary to interpret the relationships between the elements in different modes.

The first core element (1, 1, 1, 1) with a negative value (-26.6891) explains 38.87% of the core variance and the interactions between the first component (A1, B1, C1, D1) in each of the four modes. Given that all the loadings on a single component of temporal (seasons) mode (C) are negative, and all the layers under the first component of the fourth mode (D1) are positive. Hence, this core element (1, 1, 1, 1) can be explained by considering the interactions between high positive loadings of A1 (sites) and high positive loadings of B1 (chemical and biological variables) (Figures S2a and S2b), along with the positive loadings of D1. A1 (first component of spatial mode) has high positive loadings from sites S1 to S2. B1 (mode of the first component of variables) has high positive loadings on nutrients, heavy metal (Cd), and Chl *a*.

The second core element (2, 2, 2, 1) with a positive value (-14.4160) explains 9.06% of the core variance. It reflects the interactions between the second component (A2, B2, and C2) of the first, second, and third modes and a single component of the fourth mode (C). Given that C has all positive loadings and A2 has all negative loadings, the signs of B2 and D2 will determine the sign of this core element. Hence, this core element (2, 2, 2, 1) can be explained by considering the interactions between high negative loadings of B2 (temperature and pH) with negative loadings of C2 (January) (Figures 3b and 3d) along with the positive loadings of D1 and positive loadings of A2.

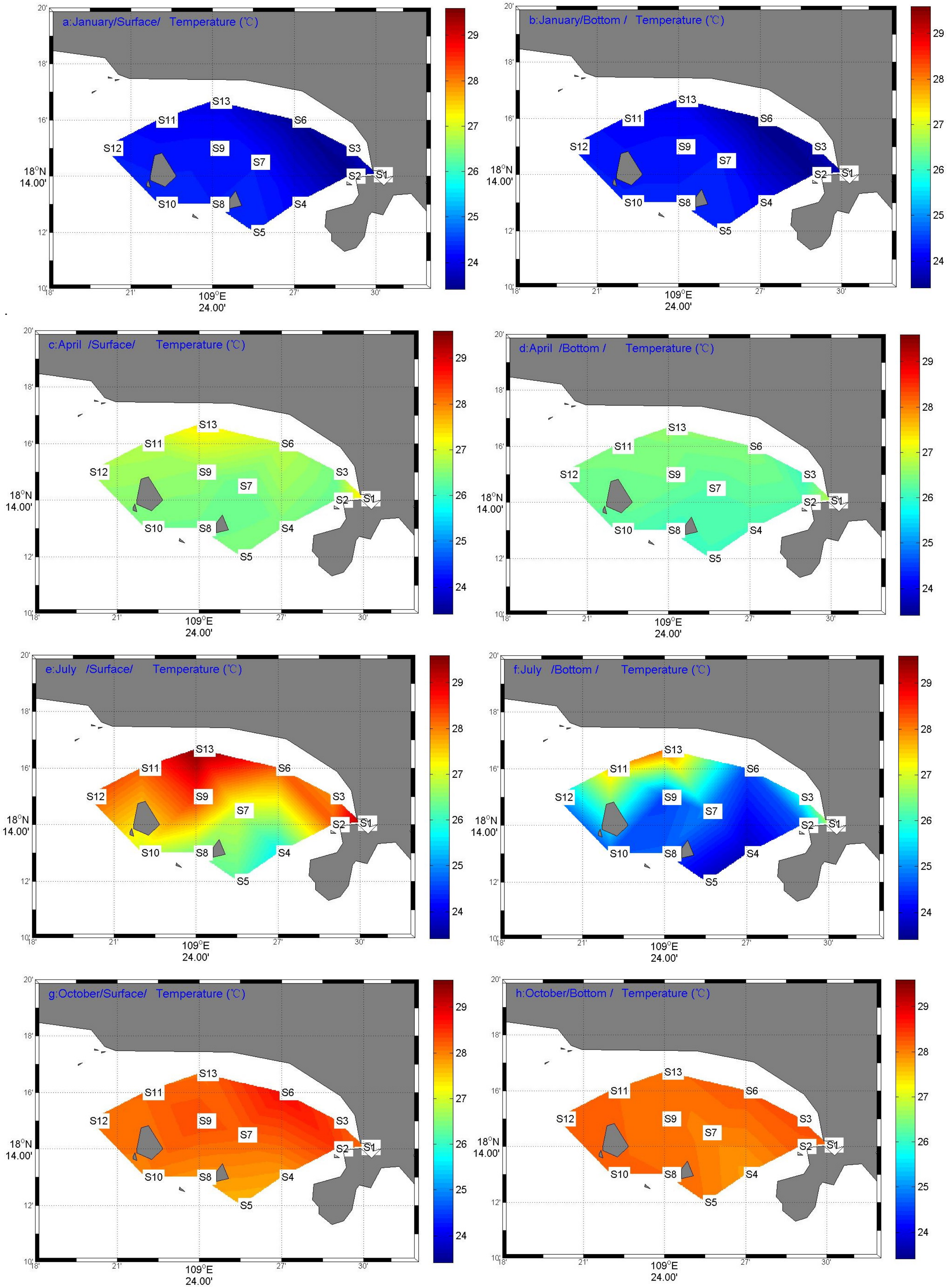

Figure 2. The spatial and seasonal changes of temperature in Sanya Bay.

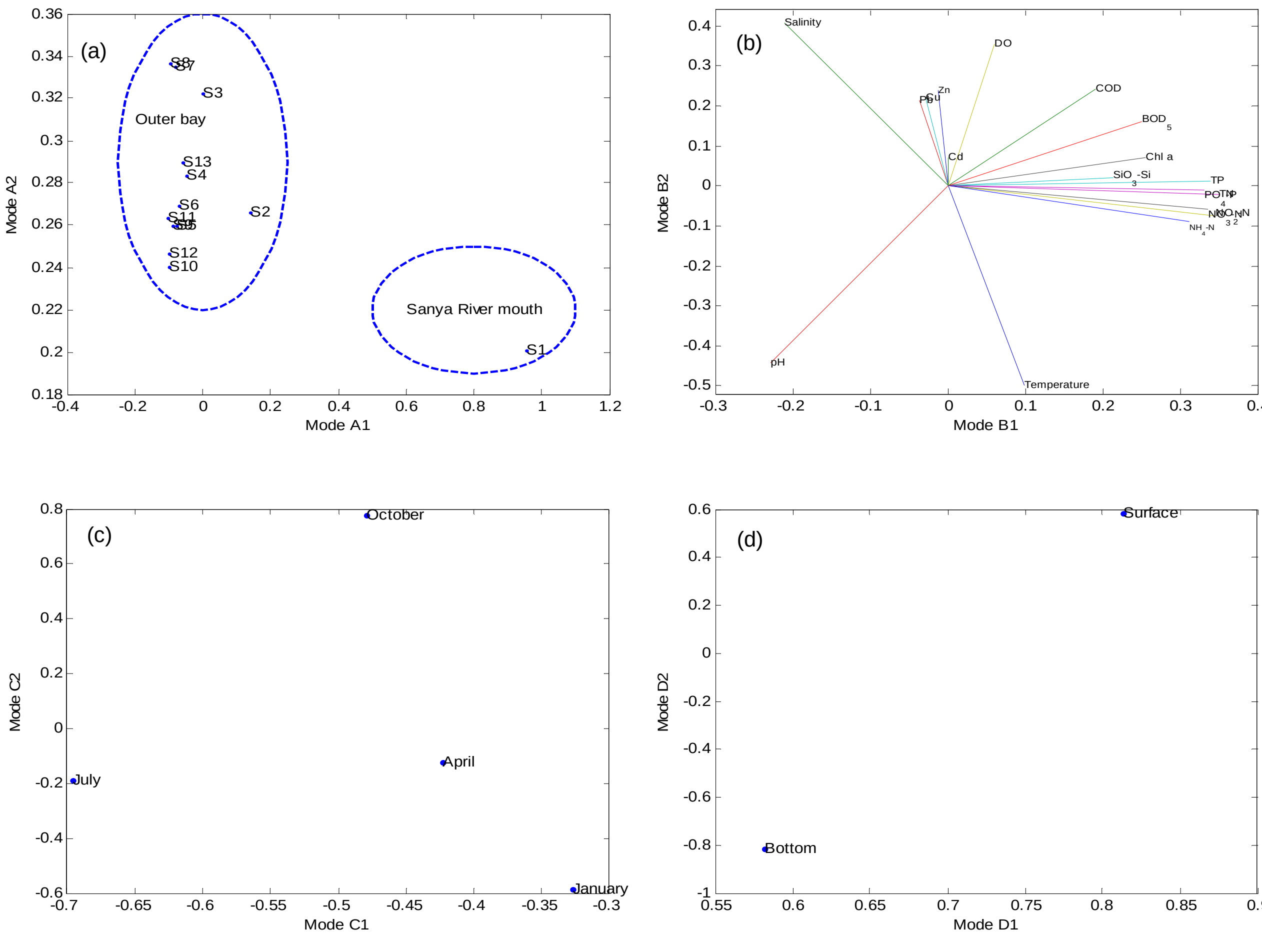

Figure 3. Plots of the first mode (sampling stations), the second mode (variables), the third mode (sampling times) and the fourth mode (sampling depths): (a) Plot of the first mode (sampling stations); (b) Plot of the second mode (variables); (c) Plot of the third mode (season change); (d) Plot of the third mode (sampling depths).

4.2. Temporal Variability

In temporal pattern, the seasonal character of the water quality is identified using weather variables (sea water or air temperature, wind direction, and precipitation) and four-way PCA (Figure 3c). Air temperature may be an important indicator of climate change. Air temperatures during the study period of May to September were higher than those in January and November (Meteorological Observatory Station of Tropical Marine Biological Research Station in Hainan, Chinese Academy of Sciences).

Sea water temperature and salinity may be important indicators of climate and marine character. The average temperature of sea surface was higher during rainy season (29.15 °C) than that during dry season (24.76 °C), with significant difference by one-way ANOVA ($p < 0.05$). The inverse relationship between temperature and DO is a natural process because warm water easily becomes saturated with oxygen, and thus, can hold less DO. During the rainy season, rain is an important factor that diminishes surface salinity (Figure S1). Fresh water from the Sanya River estuary also diminishes surface salinity. The lowest salinity appeared in autumn and the highest appeared in winter.

Precipitation is an important climate indicator of the characteristics of seasonal changes. The monthly precipitation during rainy season exceeds 100 mm and is less than 100 mm during dry season. In addition, rains often occur during the wet season. Rainfall and land-based water input may cause the difference of the water quality between dry season and rainy season.

The average concentrations of SiO_3–Si were 3.69, 3.57, 4.21, and 3.87 μmol·L^{-1} in Winter, Spring, Summer and Autumn, respectively. The concentrations of SiO_3–Si among the four seasons were significantly different ($p < 0.05$). This result is similar to that in Daya Bay. Silicate comes from land-based resources, and its rate of chemical weathering is increased particularly during rainfall (Zhu, 1999). Silicate reflects seasonal changes, and its concentration is higher during rainy season than during dry season (Huang et al., 2003), which is related to the decomposition of organic matter when temperature increases (Wu and Wang, 2007). Higher concentration of SiO_3–Si is introduced in the bay by rivers and sewage discharges during the southwest monsoon period. The high metal concentration (Zn) during rainy days may be attributed to the inputs of freshwater runoff and suspended matter from land. The seasonal variations in metal concentrations can also be related to the cycles of convection or stratification within the bay (Chen et al., 1999).

The hydrodynamic conditions of the bay are controlled by meteorological forces. The Chl *a* concentration at the bottom layer increased sharply and significantly exceeded that on the surface layer (Figure S5). During the stratification event (July), the total *chl a* concentration at the bottom layer was significantly higher than that on the surface (Zhang et al., 2010). The stable water during summer can facilitate the release of nutriants from the sediment to the overlying water, supplying algal growth at the bottom layer (Wang et al., 2003). The bay is also affected by cold-water upwelling occurring from June to August (Dong et al., 2002; Huang et al., 2003).

The seasonal changes in water quality are similar between subtropical Daya Bay (Wu and Wang, 2007; Wu et al., 2009b) and tropical Sanya Bay (Dong et al., 2010; Dong et al., 2010).

4.3. Spatial Variability

With regard to the spatial pattern, the result from the loadings of the station in mode A1 and A2 demonstrated that the two different regions of stations were well distinguished (Figure 9a). The zonation was governed by a combination of specific date and hydrographic conditions with the intervention of meteorological events. A thermocline was caused by solar irradiation in May and by the exotic cold-water upwelling from June to August. The thermocline disappeared from September to March, and then the seawater mixed (Dong et al., 2002; Huang et al., 2003). The strong stratification events occurred in the bay during southwest monsoon. The temperature at the bottom layer was lower than that on the surface layer (Figure 2). The temperature was uniform in the bay, due to the fact that water column is vertically well mixed during northeast monsoon. These physical characteristics have a significant effect on large spatial variability, in which environmental processes, such as meteorological events and water exchange from the northern South China Sea, represent exogenous inputs that strongly determine the spatial behavior of the system. Salinity had strong negative and positive loadings in modes A1 and A2, respectively. Fresh water from the Sanya River diminished the surface salinity in the monitoring site (S1). The negative correlation between nutrients and salinity demonstrate that land sources are the main reason for high levels of nutrients (Liu et al., 2005).

Domestic and industrial wastewaters are discharged into the Sanya River, and then into the bay. The monitoring site (S1) was mainly affected by domestic wastewater and runoff of freshwater of Sanya River. Both PO_4-P and SiO_3-Si concentrations decreased from east to west, probably as a result of the effects of land sources and the Sanya River (Huang et al., 2003), diluting the concentration of nutrients (pollution) from the waters of the South China Sea. Nutrient concentrations increased shoreward and clearly demonstrated the effect of the terrestrial input and the Sanya River (Zhou et al., 2009). These results showed that anthropogenic influence has an important effect on water quality in the bay.

The area in Sanya River mouth (S1) was affected by anthropogenic influence (high nutrients and low salinity) in Figure 3a. By contrast, the area in the outer bay (S2–S13) located around the western, northern, and eastern parts of the bay, and was affected by oceanic water in Figure 3a. Water quality in the Sanya River mouth was mainly affected by Sanya River, and water quality in other areas were mainly affected by the waters from the South China Sea (Dong et al., 2010; Dong et al., 2010).

5. Conclusions

The results of a classical PCA can be difficult to interpret because the information can be mixed. However, a four-way PCA is preferred because it directly takes into account the four-way structure of the data, allowing an easy interpretation of the results. The four-way PCA offers detailed information about the data set, allows visualization of the data structure, and provides an easy interpretation of spatial and temporal phenomena taking place in the region.

As a result, the main difference among the stations was clearly related to anthropogenic influence and marine characteristics. Anthropogenic influence and natural processes affected the tropical Sanya Bay in the northern part of the South China Sea. This phenomenon led to the temporal and spatial differences of water quality in the bay. Anthropogenic activities were the dominant factor that affected the water quality in the Sanya River mouth (S1). This region exhibited the maximum effect of the discharge from Saya River, which was indicated by the higher nutrient levels and Chl *a*. Marine character like upwelling and mixing caused by monsoons were the dominant factors that affected the water quality in the outer bay. All these information may help regional agencies develop a strategy to conduct scientific plans based on marine system functions for using resources.

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Supporting Material. The supporting materials containing Figures S1 to S6 are available at http://www.iseis.org/jei/download/Supplement_201400255.pdf.

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